

# Charge ordering induces a smectic phase in oblate ionic liquid crystals

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## Abstract

We report a computer simulation study of an electroneutral mixture of oppositely charged oblate ellipsoids of revolution with aspect ratio  $A = 1/3$ . In contrast to hard or soft repulsive ellipsoids, which are purely nematic, this system exhibits a smectic-A phase in which charges of equal sign are counterintuitively packed in layers perpendicular to the nematic director.

While the phase behavior of uncharged mesogens, i.e. particles with anisotropic shape, which give rise to liquid crystalline phase behavior, is now fairly well understood [1, 2], the generalization to electroneutral mixtures of charged mesogens has received very little attention. The existing computer simulation literature on ionic liquid crystals [3] is mainly focused on so-called room-temperature ionic liquids [4, 5], and high-temperature melts of simple ionic crystals [6]. The overwhelming majority of these studies considers real molecules, ranging from fully atomistic detail to coarse-grained descriptions. There is a shortage of investigations of fundamental systems, in which the shape anisotropy and the Coulombic interactions can be described with as few parameters as possible. An important exception is the work by Avendano *et al.* [7], who studied binary mixtures of oppositely charged hard spherocylinders. While Avendano’s study is of fundamental character because spherocylinders are very well defined, it is desirable to employ a different model which can continuously vary in shape between oblate and prolate forms. This way, one can systematically investigate the structure as a function of particle shape. We therefore consider charged ellipsoids of revolution, which are uniquely defined by their aspect ratio, and which do not appear to have been previously studied. The work presented in this Letter focuses on a single aspect ratio at which very interesting phase behavior is obtained: charged oblate ellipsoids with a height-to-width ratio  $A = 1/3$  feature a charge-ordered smectic phase which has not been reported before.

## MODEL DEFINITION AND COMPUTATIONAL DETAILS

We investigate electroneutral mixtures of  $N$  oblate charged ellipsoids of revolution interacting via the recently introduced anisotropic  $\text{RE}^2$ -pair potential of Everaers and Ejtehadi [8], and Coulombic forces due to point charges located at the particle’s center. The  $\text{RE}^2$ -pair potential originates from a sophisticated overlap integral between two finite bodies each having a continuous density of sites, that interact via a Lennard-Jones potential. In contrast to the widely used Gay-Berne potential [9], which is an approximation to a linear array of Lennard-Jones particles, it reproduces both short- and long-range interaction limits of ellipsoids of arbitrary shape with high accuracy, and has the additional advantage that it is well

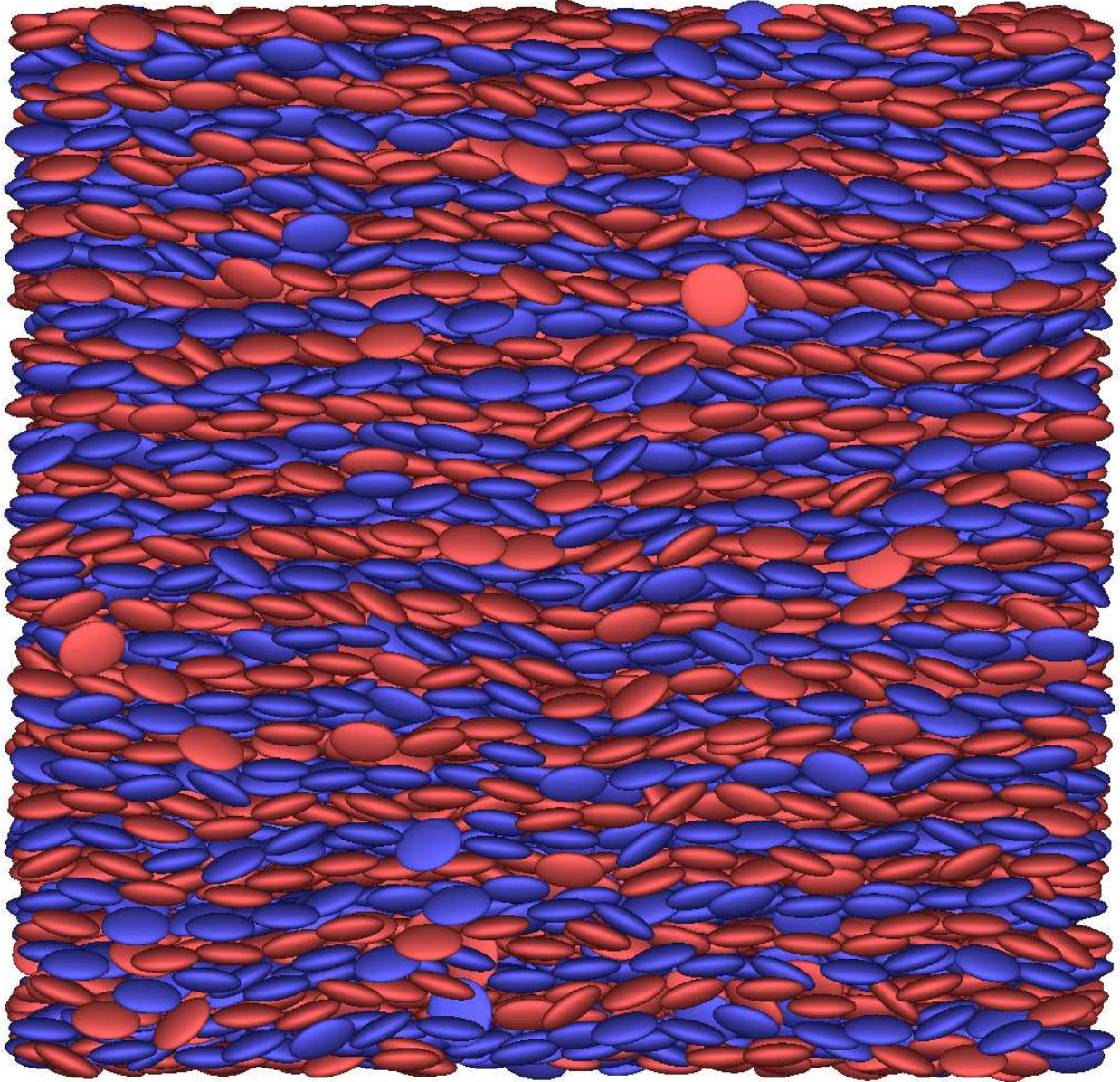


FIG. 1:

Simulation snapshot of a system with  $N = 8000$  particles at temperature  $T^* = 0.01$  and number density  $\rho^* = 0.8$ . Cations and anions are shown in red and blue. Note that the direction of the charge layers is in general oriented randomly with respect to the simulation box frame, but has been rotated here to facilitate visualization of the charge ordering.

defined and has no adjustable parameters of unclear microscopic origin. The  $RE^2$ -potential can be easily split into attractive and repulsive terms, and it is only the latter which we employ here, as we wish to study the interplay between anisotropic shape and electrostatic

interactions. Instead of quoting the lengthy expression for the orientation dependent potential here, we refer the reader to Eq. (36) of [8]. The particle shape is defined via a matrix  $\mathcal{S} = \text{diag}\{a, b, b\}$ , where  $a$  is the short radius along to the axis of revolution, and  $b$  is the conjugate radius defining the lateral elongation. Because we retain only the repulsive part of the Everaer-Ejtehadi potential, it becomes necessary to parameterize the spatial extension of the ellipsoidal particles in order to define the length scale of the the system. We chose to keep the original parameters and scale the shape-matrix  $\mathcal{S}$  with an additional factor  $s$ , which is chosen such that, in the special case of a spherical particle with  $\mathcal{S} = s \times \text{diag}\{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ , the value of the repulsive pair potential attains  $1\epsilon$  at a particle separation of  $1\sigma$ . The required value  $s \simeq 0.35492675\sigma$  was determined numerically. Defining the aspect ratio  $A = a/b$ , we chose  $a = \frac{1}{2}A^{2/3}$  and  $b = \frac{1}{2}A^{-1/3}$ , which fixes the occupied volume fraction, irrespective of the aspect ratio, to be the same as that of an equivalent system of “unit spheres” with  $A = 1$  [10]. Here, we study mildly oblate particles with  $A = \frac{1}{3}$ . The length and energy scales,  $\sigma$  and  $\epsilon$ , are henceforth used to quote all results in the usual set of reduced units [11]: number density  $\rho^* = N/V\sigma^3$ , temperature  $T^* = k_B T/\epsilon$ , energy  $E^* = E/\epsilon$ , pressure  $p^* = p\sigma^3/\epsilon$ , and time  $\tau = t\sqrt{\epsilon/m\sigma^2}$  with  $m = 1$ .

Simulations were carried out with the MD package LAMMPS [12], suitably modified to incorporate our specific potential. The RE<sup>2</sup>-potential was cut off at  $2\sigma$ . Coulomb interactions were handled using both Ewald [13] and Particle-Particle Particle-Mesh [14] summation techniques with conducting boundary conditions, and real-space cutoff of  $5\sigma$ . The system size for the numerical results reported here is  $N = 1000$ , however, we have carefully checked system size dependencies up to  $N = 32768$  and found no significant difference. In addition, we cross checked the validity of the MD results with Monte Carlo simulations using the Wolf method [15] to handle Coulomb interactions, obtaining quantitative agreement. Because the Wolf method is a direct summation technique with no long-range correction, we can thus rule out artificial stabilization of the observed phases via the reciprocal space long-range correction. The equations of motion were integrated with the Velocity-Verlet scheme using a reduced time step  $\delta\tau = 0.0075$  in the  $NVT$ -ensemble with Nose-Hoover thermostating. In order to accurately determine transition temperatures between different phases, a careful annealing procedure was followed: initial configurations were chosen randomly at a dilute concentration of  $\rho^* = 0.01$ , and the system was slowly adjusted during  $10^4\tau$  at  $T^* = 0.3$  to the desired target number density  $\rho^* = 0.8$  (corresponding to an occupied volume fraction

$\phi \simeq 42\%$ ) by isotropically decreasing the box boundaries every time step by an amount proportional to the box volume. Subsequently, the temperature was gradually decreased in intervals of  $\delta T^* = 0.005$  over  $2000\tau$ , followed by a further equilibration period of  $2000\tau$ . Data for analysis was then collected during a production run of length  $5000\tau$ . The total number of simulation time steps required for all temperatures was thus  $\simeq 53 \times 10^6$ .

## RESULTS

At the number density considered here, the system exhibits a finite value of the nematic order parameter  $P_2$  across the temperature range considered,  $T^* = 0.03 - 0.3$ .  $P_2$  is defined as the largest eigenvalue of the ordering tensor  $S_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N \frac{1}{2}(3e_{i\alpha}e_{i\beta} - \delta_{\alpha\beta})$ , where  $\alpha, \beta = x, y, z$  are the indices referring to the space fixed frame,  $\delta_{\alpha\beta}$  is the Kronecker delta, and  $e_{i\alpha}$  is a component of the ellipsoid orientation vector, taken to be the major axis along which the short radius  $a$  is defined. Above  $T^* \simeq 0.13$ , the system is purely nematic, with no long-range mass or charge ordering apparent. Below this temperature, a charge-ordered, smectic phase emerges, see Fig. 1. Interestingly, and quite counterintuitively, particles of the same charge are located in layers. The nematic director (the eigenvector associated with  $P_2$ ) is normal to these planes, thus defining the longitudinal axis of this phase. Naïvely, one could have expected a temperature-driven transition between a positionally disordered phase and a solid columnar phase, where stacks of alternatingly charged discoids are shifted parallel to each other, such that opposite charges are found in the transverse direction. However, we find that electroneutral mixtures of charged oblate particles feature an intermediate phase, where smectic ordering is realized in conjunction with charge ordering. Both the smectic character of this phase and the charge ordering have been verified by calculating the mass  $\rho_m(z)$  and charge  $\rho_q(z)$  density profiles along the longitudinal direction normal to the charge layers, see Fig. 2. While  $\rho_m(z)$  and  $\rho_q(z)$  show no features at temperatures  $T^* \gtrsim 0.13$ , both charge and mass ordering are evident in the temperature range  $0.1 \lesssim T^* \lesssim 0.13$ , clearly identifying a smectic phase in which mass and charge ordering are strongly coupled. At temperatures  $T^* \lesssim 0.1$ , a highly ordered phase emerges, which appears to be a crystalline solid, as will be discussed below. We note at this point that the same system *without charges*, i.e. interacting only via a repulsive potential, is nematic between  $T^* = 0.3$  to  $T^* \simeq 0.04$ , and freezes into a crystalline solid upon further cooling. This is in agreement

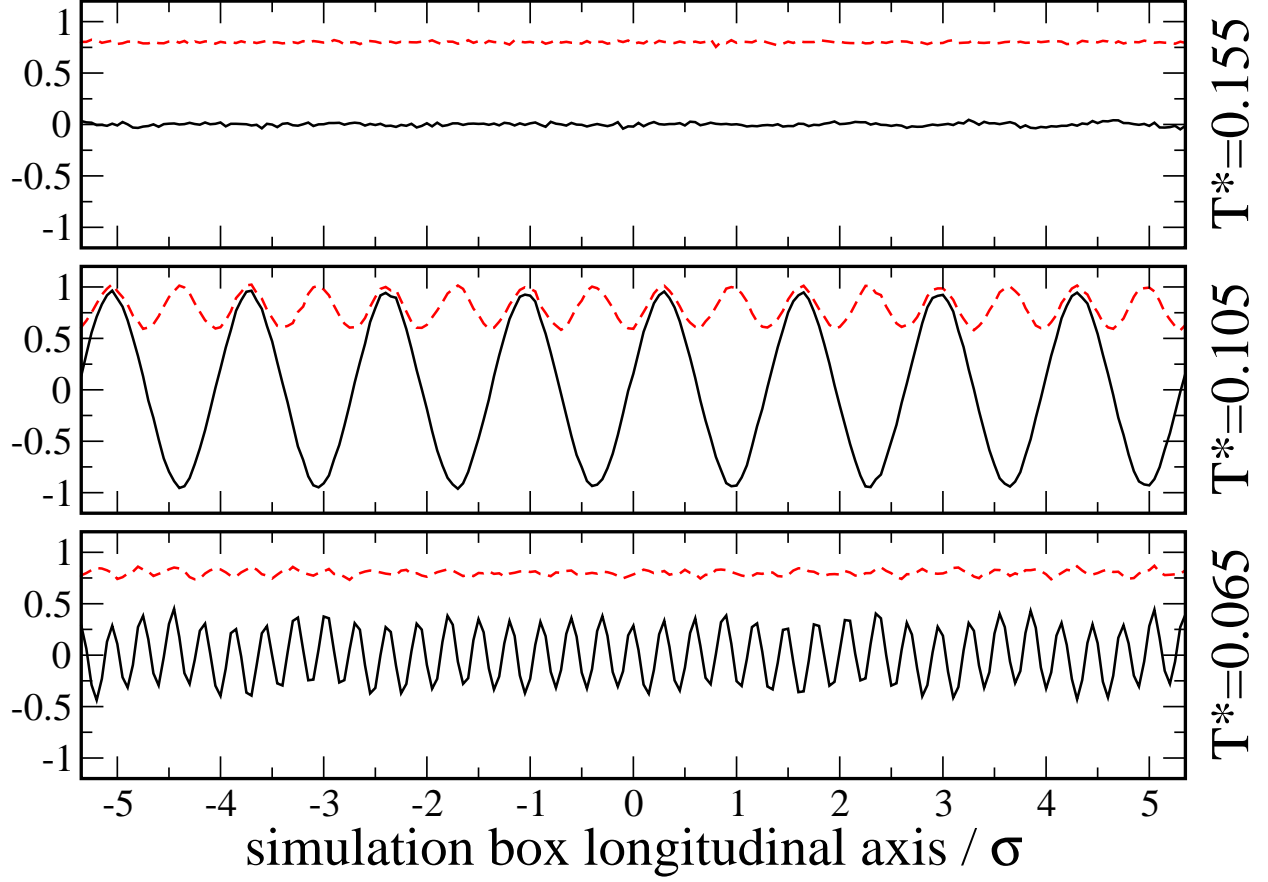


FIG. 2: Mass (dashed lines) and charge (solid lines) density profiles corresponding to the three different phases of oblate charged ellipsoids discussed here. Top: High temperature nematic phase with no charge ordering. Center: Smectic, charge-ordered phase. Bottom: Hexagonal columnar low temperature phase. The longitudinal axis of the systems is the Eigenvector associated with  $P_2$  for both the nematic and the smectic phase, while for the low-temperature columnar phase the dipole-director associated with  $P_2^d$  is used (see text). The mass (charge) density profile is calculated by summing over all masses (charges) located within a slab of width  $0.1\sigma$  normal to the longitudinal axis and dividing by the slab volume.

with theoretical considerations that hard ellipsoids do not feature a liquid smectic-A phase [16]. We thus conclude that the smectic phase we observe is induced by the Coulombic interactions. In order to quantify the degree of charge ordering, we define a charge-order parameter  $COP = \int_{-L/2}^{L/2} |\rho_q(z)| dz / \int_{-L/2}^{L/2} |\rho_m(z)| dz$ , where  $L$  is the length of the simulation box.  $COP$  attains a value close to zero for the disordered high-temperature phase and reaches values close to unity at  $T^* = 0.1$ , see Fig. 3. Below this temperature, in the

crystalline solid, the order parameter reduces to  $COP \simeq 0.2$ . This can be explained using the picture introduced above of the stacks of alternately charged discs which are shifted parallel to each other, such that particles of opposite charge are also found laterally: the shifting destroys the charge layers.

In order to quantify the correlation between ion pairs, it is instructive to consider an alternate set of local directions present in the system. For each particle, we identify the spatially closest neighbor of opposite charge. The normalized distance vector between these two particles can be regarded as a local dipole vector, and we calculate the largest eigenvalue  $P_2^d$  and associated dipole director of the ordering tensor  $S_{\alpha\beta}$  using these orientations. Analyzing these quantities, we find that there is no enhanced dipole correlation in the charge-ordered phase over the high-temperature nematic phase, see Fig. 3. However, upon further cooling below  $T^* = 0.095$ ,  $P_2^d$  and  $P_2$  increase suddenly, indicating the formation of long-range discoid stacks of alternately charged particles. This marks the transition to the low-temperature hexagonal columnar phase, which one could have expected naïvely to be the minimum energy configuration. This transition appears to be of first order, as evidenced by the discontinuities (which of course suffer from finite-size rounding effects) in both pressure  $p^*$  and potential energy  $E_{pot}^*$ .

The hexagonal columnar character of the low-temperature phase is confirmed by the hexagonal bond-order parameter  $\Psi_6$  [17], which also increases suddenly near the transition temperature  $T^* \simeq 0.095$ . The aforementioned shifting of the columns relative to each other, such that charges of opposite sign are also found along the transverse direction, is evidenced by the in-plane radial distribution functions  $g_{trans.}(r)$  shown in Fig. 4. At  $T^* = 0.105$ , the system is charge-ordered smectic, and the in-plane probability of finding a neighbor of the same charge is always higher than the probability of finding a neighbor with opposite charge. This situation is reversed at  $T^* = 0.065$ , where the system shows columnar ordering.

Interestingly, the columnar phase appears to be tilted, i.e., the orientation of the oblate particle's major axis does not coincide with the column axis. It has been recently observed [18] that attractive interactions induce the formation of tilted columnar phases in discotic mesogens. Here, we identify the columnar axis with the dipole director defined above, because, the local interparticle distance vector between spatially closest ion pairs points necessarily along the stacking direction for flat objects like the oblate particles considered here. The angle between the nematic and dipole directors increases from zero to a tilt value



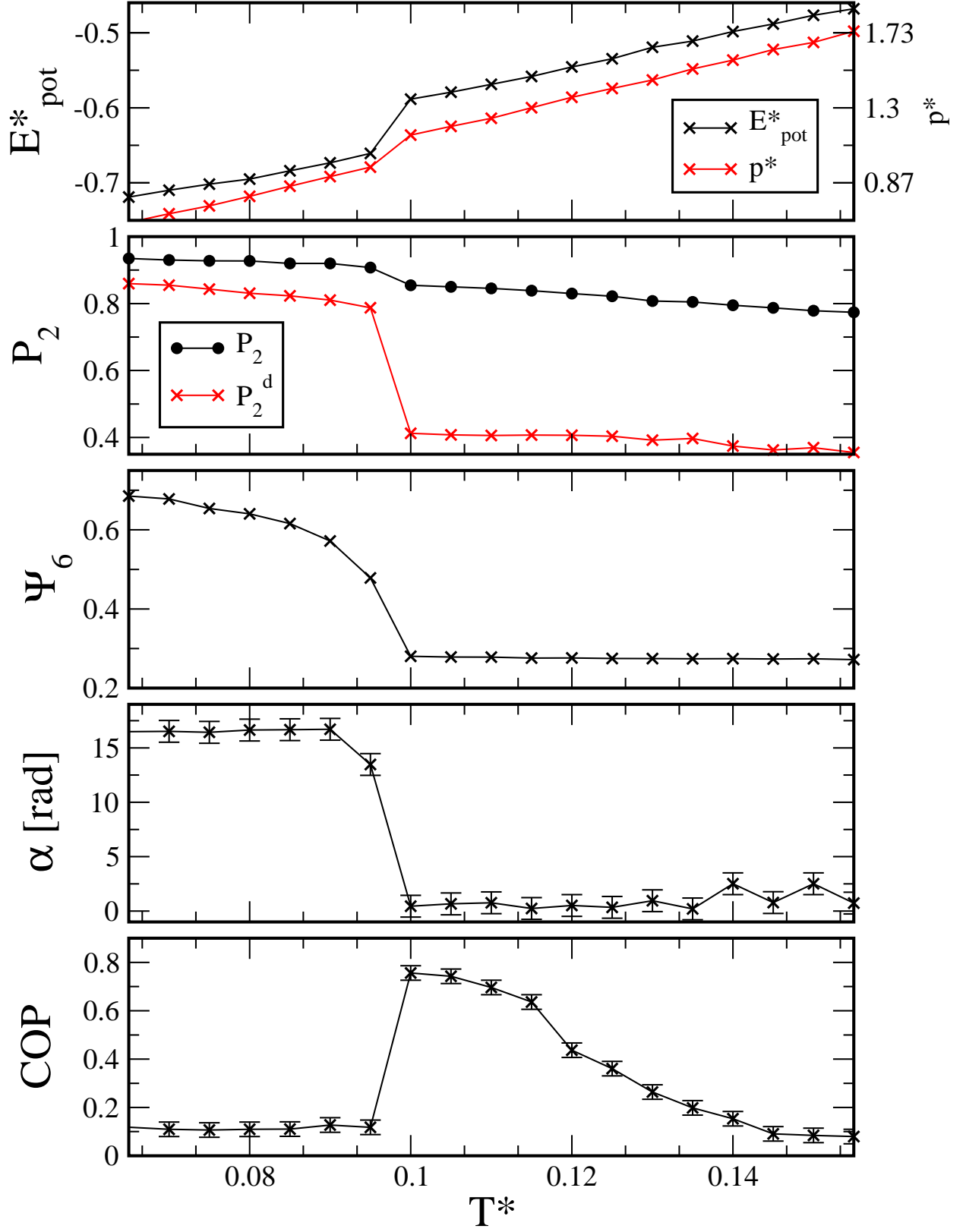


FIG. 3: Results for the order parameters (defined in the text) as function of temperature. Error bars are not shown if the symbol size is not exceeded. Note the two different ordinates for pressure and potential energy in the top graph.



of  $\alpha \simeq 16^\circ$  as the system is cooled from the liquid-crystalline smectic phase to the crystalline hexagonal columnar phase.

## DISCUSSION

We have investigated an electroneutral symmetric mixture of soft repulsive oblate ellipsoids with point charges located at the particle's center. At an occupied volume fraction  $\phi \simeq 42\%$ , we find a high-temperature nematic phase which is also known to exist in liquids of uncharged oblate mesogens [19]. In case of the symmetric Coulombic system considered here, we report, for the first time, a charge-ordered smectic liquid-crystalline phase which emerges at lower temperatures close to the freezing temperature. In this phase, particles of equal charge are organized in layers which are normal to the nematic director, such that smectic- and charge-ordering are invariably coupled. The layered arrangement yields a reasonably low energy and, at the same time, affords a relatively high configurational entropy because there is no positional order within a layer. It is this balance between enthalpy and entropy which maintains the favorable free energy, and thus stabilizes this peculiar phase. Upon further cooling, we observe a transition to a solid columnar phase which is accompanied by a shift along the column axis. The shifted phase realizes an even lower energy, but at the same time reduces entropy by enforcing positional order perpendicular to the columnar axis. The stability of the layered phase has been checked using large systems with up to 32768 particles, in order to rule out artificial stabilization due to periodic boundary effects. We note however, that for larger systems even slight undulations of the charge layers and dislocation defects (which are unavoidable due to entropic stabilization) will eventually destroy the perfect charge-ordering. Nevertheless, the properties, particularly the conductivity, of this phase promise to be interesting candidates for future studies, as the screening lengths parallel and orthogonal to the layer directions must be very different. Recent developments of colloidal synthesis techniques could make an experimental confirmation of this charge-ordered phase possible, as it is now possible to produce mesogens of continuously varying aspect ratio [20] as well as stable mixtures of oppositely charged colloids [21, 22].

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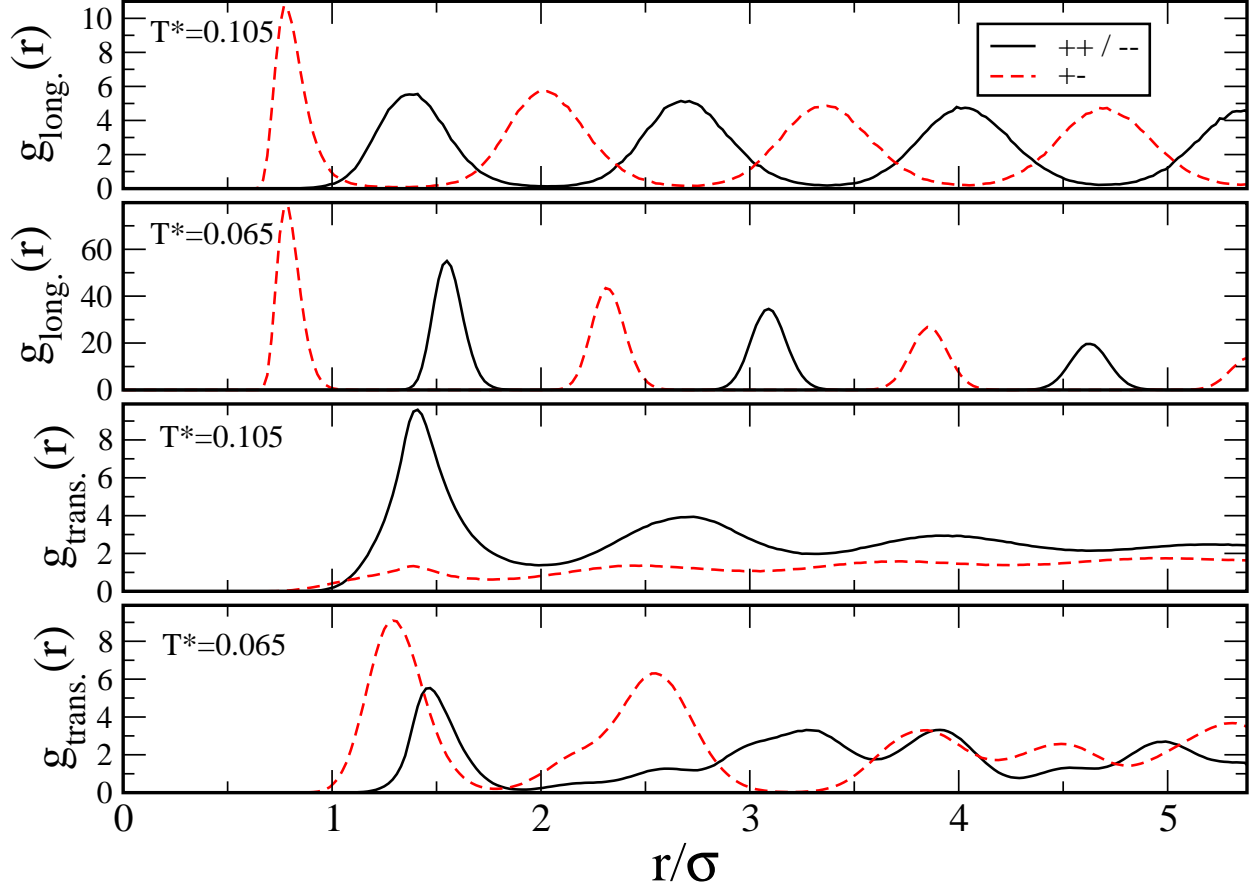


FIG. 4: Charge correlation functions  $g_{long}(r)$  and  $g_{trans}(r)$  along the longitudinal and transverse directions, respectively. Results are shown for the liquid-crystalline charge-ordered phase at  $T^* = 0.105$ , and the solid crystalline phase at  $T^* = 0.0605$ .  $++ / --$  denotes correlation functions between particles of the same charge, and  $+-$  denotes the correlation functions for pairs of opposite charge.

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